2 J
12 - B

CATALYTIC HYDROGENATION STUDIES USING COPPER CATALYSTS PREPARED BY THE RANEY METHOD

BY

JAMES A. STANFIELD

Status Report 1 - 7

Final Report

Project No. A-143

Department of the Army Project No. 5B99-01-004

Ordnance Research and Development Project No. TB2-0001

Contract No. DA-01-009-ORD-365

OOR Project Number 1107

Engineering Experiment Station

Georgia Institute of Technology

Atlanta, Georgia

1954 -55

31 March 1954

Status Report #1, Project No. A-143

Project Title:	Catalytic Hydrogenation Studies Using Copper Catalysts Prepared by the Raney Method
Contractor:	Georgia Tech Research Institute, Atlanta, Ga.
Period Covered:	January 1 through March 31, 1954
OOR Project Number:	1107
Contract Number:	DA-01-009ORD-365
Author of Report:	James A. Stanfield

I. TECHNICAL PROGRESS

The following have been accomplished:

1. An extensive literature survey of some three hundred references covering the use of various forms of copper utilized as hydrogenation catalysts for pure compounds of organic nature.

2. For comparison purposes, samples of Raney nickel catalyst have been prepared. A very pure sample of acetone has been obtained for reduction studies.

3. A brass sample, No. 1119 (60% copper, 40% zinc) was obtained and preliminary studies indicate that acid digestion with hydrochloric acid fails to give an active copper catalyst and that digestion with strong sodium hydroxide is much too slow to be satisfactory for making a Raney copper catalyst from this alloy.

II. PERSONNEL

Mr. Paul Robbins, graduate student of the School of Chemistry, has been employed as graduate research assistant on this project. Dr. James A. Stanfield, also of the School of Chemistry, has been directing Mr. Robbins as well as working with Mr. Robbins on this project.

III. FISCAL INFORMATION

During the period covered by this status report, the following expenditures have been made:

Salaries to personnel	$705.50
Overhead (45.5% of Salaries)	321.00
Materials and Supplies	125.47*
	$1,151.97

*This sum represents encumbrances against this project.

Respectfully submitted:

James A. Stanfield
Project Director

Approved:

Frederick Bellinger, Head
Chemical Sciences Division

A143

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

30 June 1954

Status Report #2, Project No. A-143

Project Title:	Catalytic Hydrogenation Studies Using Copper Catalysts Prepared by the Raney Method
Contractor:	Georgia Tech Research Institute, Atlanta, Ga.
Period Covered:	April 1 through June 30, 1954
OCR Project Number:	1107
Contract Number:	DA-01-009-ORD-365
Author of Report:	James A. Stanfield

I. TECHNICAL PROGRESS

The following have been accomplished:

1. The sample of Raney nickel, prepared as indicated in Status Report #1 of this project, has been used to hydrogenate acetone to iso-propyl alcohol over temperature range of 80-140°C and at a hydrogen pressure of 1000 p.s.i. The activation energy for the process is rather low, approximately 1600 calories per mole. The rate constant at 127°C has been found to be 27.2×10^{-4} min.$^{-1}$.

2. A sample of a copper catalyst was prepared by NaOH digestion of a commercially available granular sample of Devarda's alloy (50 copper, 45 Al and 5 Zn). A rather granular Raney-type copper catalyst was obtained which was found to hydrogenate acetone at a rate of 7.91×10^{-4} min.$^{-1}$ at 127°C. The process was found to have an activation energy of about 9600 calories per mole over the temperature range of 100 to 150° C.

3. Since the above catalyst sample was rather granular, the commercial alloy was pulverized to 100 mesh and finer on a Micro Pulverizer. A sample of catalyst prepared from this finely divided alloy appears to possess greater activity than that from the granular alloy although complete data are not yet available.

4. Three batches of finely pulverized alloys of aluminum and copper have been prepared for digestion. These contain 60, 50, and 40% copper respectively.

II. PERSONNEL

Mr. Paul Robbins is continuing as graduate research assistant on this project under Dr. Stanfield's direction.

III. FISCAL INFORMATION

During the period covered by this status report, the expenditures have been as follows:

Salaries to personnel	$761.50
Overhead, 45.5% of salaries	346.48
TOTAL	$1,107.98

Respectfully submitted:

James A. Stanfield
Project Director

Approved:

Frederick Bellinger, Head
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

30 September 1954

Status Report #3, Project No. A-143

Project Title:	Catalytic Hydrogenation Studies Using Copper Catalysts Prepared by the Raney Method
Contractor:	Georgia Tech Research Institute, Atlanta, Ga.
Period Covered:	July 1 through September 30, 1954
OOR Project Number:	1107
Contract Number:	DA-01-009-ORD-365
Author of Report:	James A. Stanfield

I. TECHNICAL PROGRESS

The following things have been accomplished during the period indicated:

1. Three batches of finely pulverized aluminum-copper alloy containing 60, 50, and 40 per cent copper by weight, have been digested under "standard" conditions to yield samples of Raney copper catalyst.

2. These catalysts have been used to hydrogenate acetone at various temperatures from 98° C to 160° C. At 155° C, the rates obtained are 16.9×10^{-4} min.$^{-1}$, 46.2×10^{-4} min.$^{-1}$, and 53.9×10^{-4} min.$^{-1}$ for the catalysts containing 60, 50 and 40 per cent copper in the original alloy.

3. The sample of Devarda's alloy, mentioned in the Status Report #2, which had been finely pulverized, was also converted to a Raney copper catalyst by digestion with sodium hydroxide and found to hydrogenate acetone to isopropyl alcohol at a rate of 45.4×10^{-4} min.$^{-1}$ at 155° C. This may be compared to a rate of 39.6×10^{-4} min.$^{-1}$ for a similar composition catalyst prepared from a less finely pulverized sample of Devarda's alloy.

4. The activation energy of the hydrogenation process was found to be approximately the same (9600 cal./mole) for all these catalysts. This is in agreement with previous report #2.

5. Preliminary experiments using nitrobenzene indicate that these catalysts will reduce nitrobenzene to aniline in quantitative yields, but require temperatures in the neighborhood of 185° C. The rate is slightly slower also. The actual rate constants have not been measured as yet since it appears that some of the Raney copper catalyst is transformed by the process. Further work is being carried out to ascertain what is the cause of this change.

II. PERSONNEL

Mr. Paul Robbins is continuing as graduate research assistant on this project under Dr. Stanfield's direction.

III. FINANCIAL INFORMATION

During the period covered by this status report, the expenditures have been as follows:

Salaries to personnel	$902.70
Overhead, 45.5% of Salaries	410.75
Supplies & materials (est)	105.00
	$1,418.45

Respectfully submitted:

James A. Stanfield
Project Director

Approved:

Frederick Bellinger, Head
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

31 December 1954

Status Report #4, Project No. A-143

Project Title:	Catalytic Hydrogenation Studies Using Copper Catalysts Prepared by the Raney Method
Contractor:	Georgia Tech Research Institute, Atlanta, Ga.
Period Covered:	October 1 through December 31, 1954
OCR Project Number:	1107
Contract Number:	DA-01-009-ORD-365
Author of Report:	James A. Stanfield

I. TECHNICAL PROGRESS

Continued experiments using a copper catalyst prepared from a 40% copper-60% aluminum alloy have indicated that the activation energy for hydrogenation of nitrobenzene to aniline is 8030 calories per mole over the temperature range of 120-205°C. At the lower temperature the rate constant was found to be 3.83×10^{-4} min.$^{-1}$ per gram of catalyst, while at the higher temperature the rate constant is 23.5×10^{-4} min.$^{-1}$ per gram of catalyst.

For hydrogenations of 1-nitropropane to n-propyl amine (achieved in excellent yields) the activation energy from 140-205°C was found to be 10,780 calories per mole. The rate constants in min.$^{-1}$ per gram of catalyst were 5.76×10^{-4} and 19.4×10^{-4}. In all these hydrogenations, a catalyst was prepared from a 60% copper-40% aluminum alloy.

It has been observed that the catalysts thus far prepared were not pyrophoric and seemed to exhibit the same activity whether used moist with

ethanol (the usual manner of storage and using Raney nickel catalysts) or whether dried and weighed prior to usage. This observation is being studied further since it is believed that greater catalytic activity would be observed if the catalyst were pyrophoric.

II. PERSONNEL

Mr. Paul Robbins continues as graduate research assistant on the project with Dr. Stanfield continuing as director.

III. FINANCIAL INFORMATION

It is estimated that the following are the expenditures and encumbrances against the project for the period covered:

Salaries	$761.70
Overhead (45.5% of salaries)	346.57
Materials and Supplies	122.00
TOTAL	$1,230.27

Respectfully submitted:

James A. Stanfield
Project Director

Approved:

Frederick Ballinger, Head
Chemical Sciences Division

Rpt.

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

5 April 1955

Status Report #5, Project A-143

Project Title: Catalytic Hydrogenation Studies Using Copper Catalysts Prepared by the Raney Method

Contractor: Georgia Tech Research Institute, Atlanta, Ga.

Period Covered: January 1 through March 31, 1955

OCR Project Number: 1107

Contract Number: DA-01-009-ORD-365

Author of Report: James A. Stanfield

I. TECHNICAL PROGRESS

Three preparations of copper catalyst were made in an attempt to obtain a more active copper catalyst. These preparations have met with some success. One catalyst, labeled 4-4, was prepared from a 60-40 aluminum-copper alloy by addition to sodium hydroxide at 50° C as rapidly as possible (three hours rather than the usual five). This was followed by a short digestion period (50 minutes) and rapid washing with water and with ethanol. A second preparation, sample 4-6, allowed only partial removal of aluminum by the sodium hydroxide at temperatures of 0° and slightly below, followed by rapid washing with water and with ethanol. A third preparation, sample 4-7, employed ice-cold base to which was added within one and one-fourth hours the usual amount of alloy. After digestion for three-fourths hour at 20° or less, the catalyst was washed rapidly. This last catalyst was found to be pyrophoric.

Hydrogenations of acetone, 1-nitropropane, styrene, nitrobenzene, and butyronitrile with each of these catalysts were carried out. Each of the catalysts was more active than any catalyst we have previously reported, factors being 2.2-2.9, 1.2-1.8, and 2.3-3.5 for the catalysts respectively.

It was found that butyronitrile was reduced to the amine only with difficulty. Temperatures of 220° C were found to give only poor yields of amine and the reaction was very slow.

Activation energies for compounds not previously reported are 9390 cal./mol for butyronitrile and 14,950 cal./mol for styrene.

II. PERSONNEL

Mr. Paul Robbins continues as Graduate Research Assistant on the project with Dr. Stanfield continuing as Director.

III. FINANCIAL INFORMATION

The following expenditures and encumbrances against the project for the above period are estimated to be:

Salaries to Personnel	$646.00
Overhead, 58% of Salaries	374.68
Supplies	65.00
	$1,085.68

Respectfully submitted:

James A. Stanfield
Project Director

Approved:

Frederick Ballinger, Head
Chemical Sciences Division

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

June 30, 1955

Status Report No. 6, Project A-143

Project Title:	Catalytic Hydrogenation Studies Using Copper Catalysts Prepared by the Raney Method
Contractor:	Georgia Tech Research Institute, Atlanta, Ga.
Period Covered:	April 1, 1955 through June 30, 1955
OOR Project Number:	1107
Contract Number:	DA-01-009-ORD-365
Author of Report:	James A. Stanfield

I. TECHNICAL PROGRESS

Catalyst samples 4-4, 4-6, and 4-7 have been analyzed for metallic content and contain 5.5, 49.5, and 34.3 per cent Al respectively, the remainder (except for 1 per cent insoluble) being copper. Of these, catalyst 4-7 is most active. The time of preparation for this catalyst has been shortened by addition of n-octanol which retarded foaming during addition of alloy to caustic.

While the ethylenic bond of styrene has been found fairly easily reducible with these catalysts, the C to C double bond of cyclohexene, cinnamic acid (trans), and maleic anhydride have been rather resistant to addition of hydrogen. This is rather surprising and work is continuing with these substances.

II. PERSONNEL

Mr. Paul Robbins continues as Graduate Research Assistant with Dr. Stanfield continuing as Director of the project.

III. FINANCIAL INFORMATION

Expenditures and encumbrances for the above period are estimated to be:

Salaries	$727.40
Overhead	421.90
Supplies	35.00
	$1,184.30

Respectfully submitted:

James A. Stanfield
Project Director

Approved:

Wyatt C. Whitley, Acting Head
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

October 10, 1955

STATUS REPORT NO. 7, PROJECT A-143

Project Title: Catalytic Hydrogenation Studies Using Copper Catalysts Prepared by the Raney Method

Contractor: Georgia Tech Research Institute, Atlanta, Georgia

Period Covered: July 1, 1955 through September 30, 1955

OOR Project Number: 1107

Contract Number: DA-01-009-ORD-365

Author of Report: James A. Stanfield

I. Technical Progress

Studies during the report period indicated above include: 1) the change of catalyst activity with time; 2) hydrogenation at various temperatures of maleic anhydride, fumaric acid, pentene-2, propionaldehyde, benzaldehyde, alpha-pinene, d-limonene, allyl alcohol, and mesityl oxide; 3) determination of activation energies for the hydrogenation of these compounds (except maleic anhydride and fumaric acid) and for cyclohexene.

It has been found that the activity of a given catalyst decreases on the order of fifty (50) percent within a period of nine (9) months.

Activation energies and rate constants per gram of catalyst at 127° C are given in the table below. In the case of alpha-pinene and of d-limonene the values given are extrapolated values since these materials were not hydrogenated at a measurable rate at the temperature indicated.

Table I.
Activation Energies and
Rate Constants

Compound	Eact. cal/mol	K/g x 10^4, 127°C	Products
cyclohexene	1400	3.84	Cyclohexand
pentene-2	4300	10.06	Pentane
propionaldehyde	14700	23.3	n-propyl alcohol
benzaldehyde	7100	30.9	Benzyl alcohol
d-limonene	5300	4.98	*
a-pinene	8700	1.40	*
allyl alcohol	6600	33.9	n-Propyl alcohol
mesityl oxide	8500	55.4	4-methyl pentanone-2 (mainly)

* Further work in progress

II. Personnel

Mr. Paul Robbins continues as Graduate Research Assistant with Dr. Stanfield continuing as Director of the Project.

III. Financial Information

Expenditures and encumbrances for the above period are estimated to be:

Salaries	$ 769.31
Overhead (58% of Salaries)	446.20
Supplies	11.70
Total	$1227.21

Respectfully submitted,

James A. Stanfield
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

FINAL REPORT

PROJECT NO. A-143

CATALYTIC HYDROGENATION STUDIES USING COPPER CATALYSTS PREPARED BY THE RANEY METHOD

by

JAMES A. STANFIELD

- o - o - o - o -

DEPARTMENT OF THE ARMY PROJECT NO. 5B99-01-004
ORDNANCE RESEARCH AND DEVELOPMENT PROJECT NO. TB2-0001
CONTRACT NO. DA-01-009-ORD-365
OOR PROJECT NUMBER 1107

- o - o - o - o -

JANUARY 1, 1954 through DECEMBER 31, 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

FINAL REPORT

PROJECT NO. A-143

CATALYTIC HYDROGENATION STUDIES USING COPPER CATALYSTS PREPARED BY THE RANEY METHOD

by

JAMES A. STANFIELD

- o - o - o - o -

DEPARTMENT OF THE ARMY PROJECT NO. 5B99-01-004
ORDNANCE RESEARCH AND DEVELOPMENT PROJECT NO. TB2-0001
CONTRACT NO. DA-01-009-ORD-365
OOR PROJECT NUMBER 1107

- o - o - o - o -

JANUARY 1, 1954 through DECEMBER 31, 1955

TABLE OF CONTENTS

(Continued)

TABLE OF CONTENTS (Continued) Page

This Report Contains 54 Pages

LIST OF FIGURES

LIST OF TABLES

SUMMARY

A study has been made of copper catalysts prepared by the digestion of a copper-aluminum alloy with sodium hydroxide followed by washing with water and with ethanol. Several different batches of this type of catalyst were prepared, differing in relative content of copper and of aluminum, differing in the exact manner or preparation, or differing in whether or not any other element was added when the copper-aluminum alloy was made. Differences in preparation included variation of the rate of addition of alloy to the caustic solution, variation in the time allowed for digestion, variation in the temperature of digestion, and variation in the rate and time of washing.

Each of these catalysts was used to hydrogenate various organic molecules. Some nineteen different organic substances were used. Of these, only four were not hydrogenated. Activation energies for the hydrogenation process were determined in twelve cases. From the ease of hydrogenation, as measured by kinetics, the relative effectiveness of the various catalysts was determined. In each case, the nature and extent of hydrogenation was followed by determination of the product of the reaction.

The actual composition of several of the catalysts was also determined as was the change of activity of the catalyst with age.

I. INTRODUCTION

Hydrogenations with finely divided metals serving as catalytic agents have been extremely valuable tools both in the industrial production of pure and technical products and in various investigative laboratories for the syntheses of many important chemicals. Among the metals so commonly used are nickel, copper, chromium, and platinum. As a general case some 30 years ago, these metals were used either as colloidally suspended particles or as fine particles of metal. They were prepared usually by the reduction of some compound of the of the metal, such as the oxide.

In 1925, however, a new approach to catalyst preparation was advanced by Murray Raney.[1] The method consisted of preparing an alloy of the catalyst metal (notably nickel) and the amphoteric metal, aluminum. By digesting this alloy with sodium hydroxide, followed by thorough washing, the aluminum was removed and the finely-divided catalyst remained. This metal showed unusual properties for effecting hydrogenations. Since this time, such metal catalysts have been referred to as Raney catalysts. Certainly today, Raney nickel is invaluable to the chemist.

While the original patents on this method of preparation covered more metals than nickel, it was only nickel on which emphasis

1. M. Raney, U.S. Patent 1,564,787 (Dec., 1925); U.S. Patent 1,628,190 (May, 1927); U.S. Patent 1,915,473 (June, 1933); see also M. Raney, Ind. Eng. Chem., 32, 119 (1940).

was placed. Very few studies have been made regarding metals other than nickel.

Although copper in various forms has been shown to be quite versatile as catalytic material, the usefulness of a copper catalyst prepared by the Raney method has escaped attention. Two more important works referring to this form of copper metal are those of Hachihama[2] and of Faucounau[3]. The latter worker describes the preparation of an active copper catalyst made from Devarda's alloy. This catalyst, obtained by the digestion of the finely divided alloy for 12 hours with 30 per cent sodium hydroxide followed by heating and washing, was found to hydrogenate heptyne-1 and limonene rather readily. In the former case a 60 per cent yield of heptane was obtained while in the latter case only hydrogenation of the exo-double bond resulted and carvomenthene was the product. The catalyst Faucounau prepared did not, however, hydrogenate cyclohexene or alpha-pinene, though aldehydes and ketones were hydrogenated.

The purpose of this investigation was to study in more detail and in a quantitative fashion, the feasibility of using a copper catalyst prepared by the Raney method. Studies were to be made regarding the method of preparation of catalyst, variations of the alloy, and hence the catalyst itself, and also the conditions

---

2. Y. Hachihama, K. Kawata, and M. Imoto, J. Soc. Chem. Ind. Japan, 45, 297 (1942).
3. L. Faucounau, Bull. soc. chim., 5, 4, 58 (1937).

necessary to effect the hydrogenation of various organic compounds. With regard to this latter phase of the work, the approach was to be made through a study of the rate of the hydrogenation process at various temperatures. From this one would be able also to ascertain the activation energy of the hydrogenation process.

II. THEORETICAL

The process of catalytic hydrogenation, the union of hydrogen with a given compound in the presence of a catalyst, is generally effected as a heterogeneous reaction, i.e., there is more than one phase present in the reaction mixture. Adkins[4] has listed a number of requirements of a good catalyst. Such a catalyst, he states, should (1) be stable in the presence of the reactants; (2) adsorb and activate the hydrogen; (3) adsorb and activate the hydrogen acceptor; (4) hold the activated hydrogen and the hydrogen acceptor in the proper spatial relationship for reaction; and (5) desorb or set free the reaction products. Failure of a catalyst to perform these satisfactorily will result in a decrease in the effectiveness of the material as a hydrogenation catalyst.

For instance, should the catalyst not desorb the hydrogenated product rapidly, the surface of the catalyst would very shortly become covered with product, and hence no new material could be adsorbed on the surface and made available for reaction. This is, of course, the essential phenomena occurring in the poisoning of a catalyst, i.e., the catalyst surface becomes covered with strongly adsorbed materials other than reactants.

---

4. H. Adkins, Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts (Madison: The University Press, 1937), p. 9.

Frequently, however, it is observed that trace quantities of foreign materials may enhance the activity of a given catalyst. Such materials are commonly designated as promotors. These may act by increasing the number of active centers (due to increasing the number of crystal faces, edges, corners, etc.); by furnishing an interface at which adsorption takes place; by increasing the velocity of activated adsorption processes; by changing the ratio of adsorption of the two reactants; by activating one reactant which the catalyst did not activate sufficiently; or, by modifying the nature of the orientation of the catalyst crystals.[5]

In addition to these factors, the conditions under which the catalyst is prepared also will influence its activity as a catalyst. In the case of Raney catalysts, the temperature and speed of digestion, and the extent and speed of washing are also significant. In other words, any condition which may alter the nature of the surface of the material will affect the usefulness of that material as a catalyst. However, it should be pointed out that while the extent of a catalyst surface may be important, of greater importance is the nature of that surface. Merely because a substance has a great surface area does not mean per se that the material is a better catalyst than a similar substance having a smaller surface area.

5. H. B. Weiser, Colloid Chemistry (New York: John Wiley and Sons, Inc., 1946), p. 51.

In order to ascertain the effectiveness of any material as a catalytic agent, it is necessary to determine in some manner the ability of the substance to bring about the given reaction. In the case of hydrogenations, the most reliable method of achieving this is by determinations of the rates of the reaction. Through this important area of chemical kinetics, the rates of reactions and the various factors influencing these rates may be studied. From such a study it may able to postulate not only the optimum conditions for effecting the reaction, but also the mechanism by which the reaction occurs.

A. The Reaction Rate

From a quantitative standpoint, it is useful to define the order of reaction as the number of atoms or molecules whose concentration will determine the rate of the reaction. Thus, in the reaction

$$aA + bB \rightarrow C \qquad (1)$$

the rate of disappearance of A, -dc/dt, is dependent upon both A and B concentrations. This may exactly be defined by

$$-\frac{dc}{dt} = k\,[A]^a[B]^b, \qquad (2)$$

in which c is the concentration of A, t is the time in minutes, and k is the reaction rate constant.

The exponents, a and b, are the orders of the reaction with respect to the reactants, A and B, respectively. Their sum, a + b, is the total order of the reaction.

In catalytic hydrogenation, it has been shown by Smith and co-workers[6] from studies on the hydrogenation of the benzene nucleus that the reaction is independent of the hydrogen acceptor concentration (i.e., zero order), is first order with respect to hydrogen, and is directly proportional to the amount of catalyst used. Hence, in Equation 2, one may neglect the reactant B (the acceptor in hydrogenations). Then substituting c for the concentration of A, one obtains

$$-\frac{dc}{dt} = k\,c \quad . \tag{3}$$

Upon integration and conversion to common logs, one obtains

$$\log \frac{c_1}{c_2} = \frac{k\,(t_2-t_1)}{2.303} \quad , \tag{4}$$

where c_1 is the concentration of A at time t_1 and c_2 that at t_2. Now if one replaces c_1 with c_o (the initial concentration of A at the initial time, t_1) and lets c_2 become the concentration of A at time t, equation 4 becomes

---

6. H. A. Smith, D. M. Alderman, and F. W. Nadig, J. Am. Chem. Soc., 67, 272 (1945); H. A. Smith and E. F. H. Pennekamp, J. Am. Chem. Soc., 67, 276 (1945); H. A. Smith and J. A. Stanfield, J. Am. Chem. Soc., 71, 81 (1949); and subsequent papers.

$$\log \frac{c_o}{c} = \frac{kt}{2.303}, \qquad (5)$$

since t_1 is zero. In hydrogenations, the reactant A is gaseous, the concentration is proportional to the pressure of A, and one may substitute pressures for concentrations:

$$\log \frac{p_o}{p} = \frac{kt}{2.303} \qquad (6)$$

Obviously this is the equation for a straight line, and if one plots log (p_o/p) versus t, one obtains a straight line, the slope of which is $k/2.303$. The rate constant, k, therefore, may be obtained from the expression: k = 2.303 times the slope.

In this work, the rate of the reaction was followed by determination of pressure changes with time. From graphing these data in the manner just described, the rate constant could be calculated. The value thus obtained was divided by the weight of the catalyst used, in grams, giving the units of k as reciprocal minutes per gram.

B. The Effect of Temperature on the Rate Constant

The Arrhenius equation expresses the change in the rate constant with temperature:

$$\frac{d \ln k}{dt} = \frac{E_a}{RT^2} \qquad (7)$$

where k is the rate constant, T the absolute temperature, R the universal gas constant in calories per mole, and E_a the activation energy for the reaction.

Upon integration, one obtains

$$\ln k = -\frac{E_a}{RT} + C, \tag{8}$$

or in common logarithms,

$$\log k = \frac{E_a}{-2.303\ RT} + C. \tag{9}$$

This is also the equation for a straight line, and a plot of log k versus 1/T will give a straight line of slope $-E_a/2.303R$. Thus the activation energy of the process, E_a, may be calculated.

Another integrated form of the Arrhenius equation is

$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303\ R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{10}$$

In this equation, k_2 and k_1 are the rate constants at T_2 and T_1 respectively. This equation has been found quite useful in calculation of the reaction rate constant at a desired temperature provided there is known the activation energy of the reaction and the rate constant at some known temperature.

C. The Effect of Volume on the Rate Constant

Smith and Fuzek[7] have pointed out that all too frequently observers fail to report the volume of the vapor phase in hydrogenations. They were able to show that the rate constant is inversely proportional to the volume of the gas. The more correct form of the rate equation should be

$$\log \frac{p_o}{p} = \frac{k\ t}{2.303v}\ , \qquad (11)$$

where v is the volume of the hydrogen void.

Thus, if rate constants are to be comparable, the volume of the gas phase should be the same, or else the obtained rate constants should be multiplied by a volume factor. In this work, since the same hydrogen void was employed in all studies, the rate constants obtained are comparable with each other. They have not been multiplied by the hydrogen volume of the system. However, in comparing these results with those of others, the rates reported herein should be multiplied by the volume, 44.8 ml, and unless already reported as such, the results of other investigators should be multiplied by the hydrogen void encountered in their work.

---

7. H. A. Smith and J. F. Fuzek, J. Am. Chem. Soc., 70, 3743 (1948).

D. The Effect of Solvent

The role of the solvent has been shown to have a pronounced effect upon catalytic phenomena. However, in this work, the compound itself served usually as the solvent. Thus, this particular factor need not be discussed at this point.

III. APPARATUS

A. The Hydrogenation Apparatus

A high-pressure micro shaking mechanism, complete with shaker, heating jacket, reaction vessel, valve, and gage was obtained from the American Instrument Company, Silver Spring, Maryland.

The shaking mechanism had a heavy cast iron base on which was mounted a one-bearing pedestal for supporting an oscillating trunnion. A heating jacket was clamped to the trunnion and the removable reaction vessel fitted inside the heating jacket. The gage and valve were mounted directly on the head of the vessel. Agitation was accomplished by a 1/8-horsepower motor mounted on the base. The vessel was rocked through an arc of about 30 degrees at a rate of 34 cycles per minute.

The reaction vessel used was either a manganese steel composition or 18-8 stainless steel composition. In either case the outside dimension was 2 9/16 in. and the inside diameter 3/4 in. with an inside depth of 6 in. A thermowell was bored into the wall of the vessel, 5 in. upwards from the bottom. The compression closure consisted of four parts: (1) the outside cap which screwed on the reaction vessel; (2) thrust bolts; (3) a hardened steel ring which kept the thrust bolts from marring the pressure head, and (4) the inner pressure head with a flat copper or stainless steel

gasket. The valve fitted into this inner head and the gage screwed into the valve, completing the assembly. All gas connections were made with superpressure tubing. The gage used in this assembly was 4 1/2 in. in diameter, and was graduated in intermediate graduations of 20 psi with a pressure range of 0 to 5000 psi.

A vise was made which held the vessel upright, the grooves in the bottom of the vessel fitting in the vise socket. This device greatly facilitated the removal and assembly of the cap and head from the vessel.

Pyrex glass liners were necessary in this work to prevent contamination of the hydrogenation mixture. These were obtained on special order from the Consolidated Glass Works of Kingsport, Tennessee. These liners were constructed so as to fit snugly inside the reaction vessel. They were equipped with interchangeable ground glass stoppers. Each liner had a small hole on the side, about two-thirds the way up from the bottom.

In order to insure that each thrust bolt was uniformly tightened, a torque wrench was used.

Inasmuch as the reaction vessel and its contents had to be heated, it was necessary that some control beyond the "low-medium-high" control of the heating jacket be used. For this purpose, therefore, the incoming voltage from the usual 110-volt line was first led into a constant voltage transformer and thence to Variac and thence to the heating jacket. By means of the Variac and con-

trol of the input voltage, the jacket could be heated at any rate and the temperature maintained uniformly throughout any reaction. The temperature was ascertained by a Weston dial-type thermometer which was inserted into the thermowell of the reaction vessel.

B. The Furnace for Preparation of the Alloys

A small electric furnace, the Handi-Melt Electric Furnace, was used in preparing the alloys. This furnace was obtained from the A. S. Lapine and Company.

C. The Pulverizing Equipment

After the alloy was prepared, it was necessary to grind the material to a fine powder before digestion. For this purpose a Mikro Pulverizer was obtained from the Pulverizing Machinery Company of Summit, New Jersey. This apparatus, known as a Bantam-type, pulverized the alloy samples by impact grinding. In order to obtain sufficiently fine powder, a screen, number 027 RD 24G was used. The powdered alloy was sufficiently fine to pass a 200-mesh screen.

D. The Fractionating Column

Since all reactants had to be carefully purified before use, a small column, packed with small tantalum Podbielniak spirals, was employed for all distillations. The column, 20 in. in length, was equipped with a 50 ml or a 25 ml distilling pot. The head of the column was of the total-reflux, partial take-off type. While

actual determination of the number of theoretical plates of the column was not made, the manufacturer of the packing claimed approximately 40 plates for a column of this size.

In handling very small amounts of products, the above column could not be used. In its place was substituted a Vigreux type column, 18 in. in length and having a diameter of 7/16 in. This column, having about 6 theoretical plates, had an extremely small hold-up (about 0.2 ml).

IV. MATERIALS AND METHODS

A. The Metals

All the metals used for preparation of the catalysts were C. P. materials. Each particular metal was purchased in sufficient quantities at the beginning of the work so that a single batch preparation from the manufacturer would be available for the entire project. In this way, variations due to slightly different starting materials would be avoided.

B. The Compounds

It was necessary in the work to be certain that all compounds hydrogenated be as pure as possible. For this the best grade of the chemical was used, and each sample was purified carefully. Table I indicates the substances which were used during this investigation. The melting point or boiling point and the method used for the purification of the material is also given.

In addition to the organic materials listed in the table, quantities of sodium hydroxide were also needed. Chemically pure caustic was used. For all washings of the catalysts, distilled water was employed.

C. Preparation of the Catalysts

The following will illustrate a typical method for the preparation of the alloys used later in obtaining the Raney copper

catalysts. In the Handi-Melt furnace was placed 115 g. of aluminum metal. The material was heated to about 675° C, the aluminum melting slightly below this temperature (670° C). Then 115 g. of copper shot was added slowly. The temperature of the furnace was then increased until the copper had melted and had mixed intimately with the aluminum. This occurred in the neighborhood of 1050° C. The molten mass was then poured slowly into water, whereupon it formed various sized chunks of alloy. In order to be able to introduce the pieces of alloy into the worm-type feed of the Mikro-Pulverizer, it was necessary that the pieces be broken into smaller sized lumps. This was achieved by using a hammer. The alloy, after pulverizing in the Mikro-Pulverizer, passed a mesh screen. It was stored in glass bottles until needed to prepare the Raney catalyst.

D. Preparation of the Raney Copper Catalysts

Several different methods were used in preparing the copper catalysts for this work. While not all of these will be discussed in detail, all will be mentioned below and frequently referred to in the next part of this report.

For comparison of the copper catalysts with some nickel catalyst, a batch of Raney nickel catalyst was prepared according to the procedure of Mozingo[8]. This procedure was followed quite exactly, even as to amount of alloy used.

8. R. Mozingo, Organic Syntheses, Coll. Vol. III (New York: John Wiley and Sons, 1955), p. 181.

TABLE I

PROPERTIES OF COMPOUNDS USED

Compound	Method of Purification	Boiling Point and Pressure (°C/mm)	Melting Point (°C)
Acetone	Note 1	56.5/746.9	
Allyl alcohol	Dried over $CaCO_3$ then distilled	94.7-96.0/744.0	
Benzaldehyde	Distillation	175.0/730.0	
Butyronitrile	Distillation	115.8/730.0	
t-Cinnamic Acid	Recrystallization from C_6H_6		132.4-132.6
1,3-Cyclohexadiene	Note 2	80.0-82.0/740.0	
Cyclohexene	Distillation	82.0-82.4/740.0	
Diethyl ketone	Distillation	101.6/746.5	
Ethyl oleate	Distillation	203.0-206.0/742.0	
Fumaric Acid	Recrystallization from CCl_4		286-287
n-Hexane	Distillation	67.5/730.0	
d-Limonene	Distillation	175.5/730.0	
Maleic anhydride	Recrystallization from $CHCl_3$		54.0-54.5
Mesityl oxide	Distillation	127.0/730.0	
2-Methyl-2-butene	Note 3	37.8-40.0/748.0	
Nitrobenzene	Note 4	130.0/71.0	
1-Nitropropane	Note 5	52.0/159.0	
2-Pentene	Note 6	37.2/750.0	
α-Pinene	Distillation	152.0/730.0	
Propionaldehyde	Distillation	47.0/730.0	
Styrene	Distillation	143.0/730.0	

(Continued)

TABLE I (Continued)

PROPERTIES OF COMPOUNDS USED

NOTES

1. Acetone was purified by treatment of 300 ml with 2.0 g. of $KMnO_4$, shaking, then let to stand overnight. After removal of the permanganate and MnO_2, the compound was dried over $CaSO_4$ then distilled.

2. The cyclohexadiene contained 20 per cent cyclohexene.

3. The 2-methyl-2-butene was prepared by treating 25 ml of t-amyl alcohol with 16 ml of 50 per cent sulfuric acid and collecting the product which distilled. After drying over NaOH, the olefin was redistilled.

4. After washing the nitrobenzene with warm, dilute NaOH solution it was washed several times with water. Drying was effected using $CaSO_4$. The dried compound was finally distilled.

5. The 1-nitropropane was washed first with warm, dilute NaOH solution, then with water. After drying over $CaSO_4$ it was distilled.

6. The 2-pentene was prepared from 3-pentanol which in turn was obtained from diethyl ketone. Hydrogenation of 200 ml of diethyl ketone (b.p. 101.4-101.6/746.5 mm) to 3-pentanol was accomplished using Raney nickel catalyst. Twenty-five ml batches of the alcohol (b.p. 115.0-115.4/747.0 mm) were dehydrated with 5 ml of 75 per cent sulfuric acid solution to yield the olefin. After removing the olefin by distillation, it was washed thoroughly with water, then dried over NaOH. The dried product was next distilled.

Catalyst R-Cu-1[9] was prepared by grinding in a mortar some C. P. Devarda's alloy which had been supplied in coarse granules until the material was reasonably finely divided. Digestion was accomp-

---

9. Catalyst samples are coded in the following way. The prefix R stands for Raney, the Cu for the metal (or metals) present in the catalyst and the number or numbers for the batch lot.

plished by adding, with stirring, 37.5 g. of the alloy to a solution of 47.5 g. of NaOH in 187 g. of water. The addition took about two hours. Cooling was effected just as in the Mozingo method. The remainder of the preparation followed identically that of Mozingo.

The second catalyst batch, made from Devarda's alloy, R-Cu-1A, was prepared using the standard method of Mozingo. The catalyst was prepared in larger quantities, using 75 g. of alloy with 374 g. of distilled water and 95 g. of NaOH. The chief difference between catalyst 1 and 1a is that 1a alloy was pulverized using the Mikro-Pulverizer. The alloy would pass a 200-mesh screen.

Catalyst R-Cu-2 was prepared using 70.9 g. of the pulverized alloy (60 per cent Cu, 40 per cent Al), 354 g. of water, and 89.8 g. of NaOH. The time necessary to add the alloy was 1.75 hours, after which digestion continued overnight. Washing was achieved after the method of Mozingo.

Catalyst R-Cu-3, a 50-50 Cu:Al alloy base, was prepared by the standard method using 90 g. of the alloy, 114 g. of NaOH, and 450 ml of water. Complete addition of alloy took 1.8 hours. The remainder of the preparation was as usual.

While the procedure of Mozingo was followed for sample R-Cu-4 insofar as was possible, the presence of 60 per cent Al in the alloy made it slower to add the alloy to the caustic. Of the al-

loy, 90 g. was used together with 114 g. of NaOH and 450 ml of distilled water. Addition of the alloy to the caustic took five hours.

Catalyst R-Cu-4-4, made from a 40-60 Cu:Al alloy (as are all the R-Cu-4 series alloys and catalysts), was treated in a slightly different manner. The alloy (90 g.) was added to the regular amount of caustic solution which had been cooled to 50° ± 2° C. The addition, which was done as rapidly as possible and still maintain the given temperature, took 3.25 hours. The material was allowed to stand at 50° C for 50 minutes longer and then was washed in a manner similar to that used by Adkins and Pavlic[10] in their preparation of Raney nickel W-4 catalyst. Washings were neutral to perhydrion paper after twenty minutes (rate of washing was 250 ml/min). After being tested neutral, washing of the catalyst continued for 20 additional minutes. The sample was then washed three times by decantation with 95 per cent alcohol and twice with 100 per cent ethanol, after which it was stored under alcohol in the usual manner.

The method of Adkins and Pavlic for preparation of their catalyst W-4 was followed in part for R-Cu-4-6, but with the following modifications. Sodium hydroxide solution was cooled to between 0° C and 10° C and the 90 grams of alloy added to this cold solution within the space of one hour. At all times during the addi-

---

10. H. Adkins and A. A. Pavlic, J. Am. Chem. Soc., 69, 3039 (1947).

tion, the temperature of the caustic was below 50° C, the cooling being effected by means of dry ice-acetone mixture. Constant stirring was also necessary. During the addition, the temperature dropped too low and the solution froze. This required it to be warmed to -5° C. As soon as the solution melted, the excess alloy present began reacting very rapidly and considerable foaming and frothing resulted. Some of the solution overflowed from the container, resulting in a substantial loss of catalyst. By quenching the mixture, the reaction was once again brought under control, after which the digestion was completed without further mishap. Only five liters of water were required for the washing. The catalyst was then washed with alcohol in the usual way and stored in the refrigerator.

By using less alloy for the catalyst preparation and by exercising a more careful control of the cooling process, it was possible to prepare a copper catalyst, R-Cu-4-7, according to the general procedures of W-4 type nickel catalysts. For this, 70 g. of the alloy was added slowly to a well-cooled caustic solution. In order to retard excessive foaming, 2 ml of n-octanol was added to the caustic. The addition time was 1.25 hours and the temperature maintained at 20° C or less. After letting the alloy digest for 0.75 hours, the catalyst was washed by gravity, a total of six liters of water being used. Washing with water and alcohol was

accomplished in 0.5 hours. The total time of preparation was only 2.8 hours. The catalyst was more reddish in color than any of the previous catalysts and was found to be pyrophoric.

The next sample of catalyst, R-Cu-4-8, was prepared in a manner analogous to R-Cu-4-4. The only difference was the time of addition of the alloy to the caustic. This time was found to be shortened through the addition of 2 ml of n-octanol to the usual caustic solution. In this case the period of addition was only 1.25 hours as compared to 3.25 hours in the earlier catalyst.

The last batch of catalyst, R-Cu-4-9, was prepared by the method used for R-Cu-4-4 except that the time of addition of the 90 g. of alloy was shortened to 0.83 hours. A temperature of 50° C was maintained throughout the digestion. The resulting catalyst was stored in the usual way after customary washing with water and with ethanol.

E. Hydrogenation Technique

Into a glass liner of the hydrogenation bomb was added an approximate amount of catalyst. The catalyst was handled by pipetting from the catalyst storage bottle an amount of catalyst suspended in the ethanol. An ordinary piece of glass tubing was used for this work. The amount of catalyst used varied, of course, from run to run; however, less than one gram of catalyst was found to be the best amount. Too large samples of catalysts were not agitat-

ed sufficiently, and much of the material would settle to the bottom of the liner and never have access to hydrogen or hydrogen acceptor.

After the catalyst sample in the liner had settled, the excess alcohol was decanted and the moist catalyst was retained in the liner. The desired quantity of hydrogen acceptor was added to the liner by means of a pipette or hypodermic syringe. Usually a 5 ml sample was used. The liner was then placed in the bomb and the reaction vessel lowered into the table vise. After assembling the head, the thrust bolts were screwed in gradually and symetrically so that the head was tight. Hydrogen was then introduced into the bomb by means of pressure tubing leads from a cylinder of hydrogen gas. A pressure of 1000 ± 50 psi was used.

When filled, the apparatus was removed from the vise and placed carefully into the heating jacket. The heating jacket was turned on and the assembled apparatus was permitted to heat to the desired temperature. After reaching constant temperature, shaking of the apparatus was commenced.

In order to obtain the rate of the reaction, a reading of the pressure was made as soon as shaking was commenced. At regular intervals, the time and the pressure of hydrogen were obtained and recorded. This was continued for a sufficient time after which the data was plotted according to the procedure already discussed. A

typical graph of a hydrogenation is shown in Figure 1.

At the conclusion of the run, the excess hydrogen was vented, the head disassembled, and the liner with its contents were removed from the reaction vessel. The compound was separated from the catalyst by filtration through a fritted glass funnel which had previously been weighed. The catalyst was washed with a suitable solvent, and the washing was combined with the product of the reaction. The catalyst sample in the fritted funnel was placed in a desiccator and dried overnight over $CaCl_2$. When dry the funnel and its contents were weighed again, and the weight of catalyst was thus obtained. In those cases wherein the catalyst was pyrophoric, the catalyst was never permitted to become dry in the air. Instead, when filtering the catalyst from the product, dry carbon dioxide was passed over the catalyst to exclude the air. The funnel and its contents were then quickly transferred to a desiccator which was immediately filled with CO_2.

The product from the hydrogenations were reserved for analysis, usually done by fractional distillation. In some cases, however, other techniques were used. These will be discussed later.

F. Calculation of Energy of Activation

As has been discussed previously, the energy of activation for the hydrogenation can be calculated if the rate constants at various temperatures are known. A typical plot of this is shown in

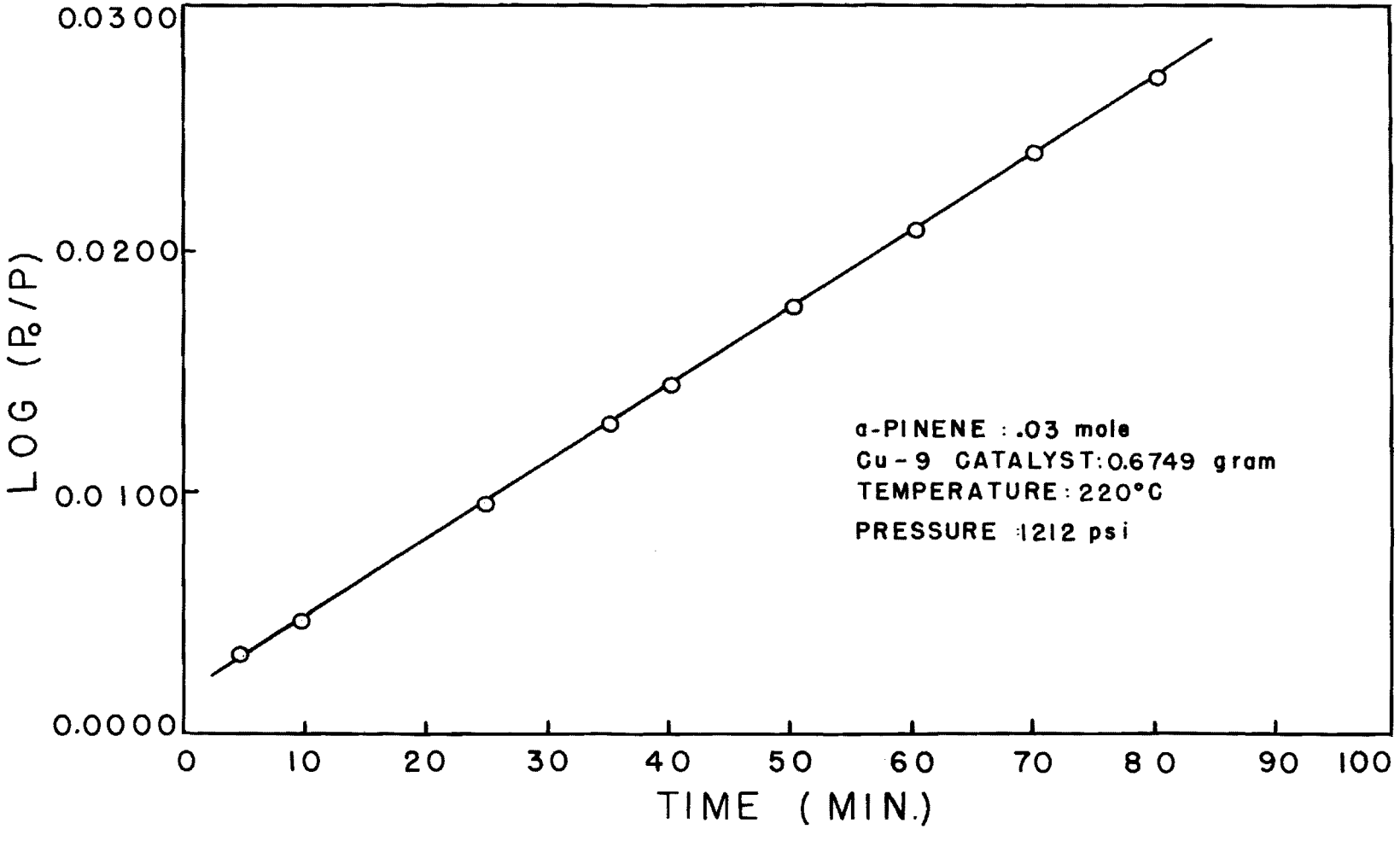

Figure 1. Sample Hydrogenation Curve.

Figure 2. In the cases where the reproducibility of the rate constants was not too good, or there was some doubt as to the exact line to draw between the various points, the slope was determined by the method of least squares.

G. Analytical Procedures

The methods employed for analysis of the products of the reduction is discussed under the individual compound in a later section.

The analysis of the catalysts for copper and for aluminum content were achieved by first dissolving the catalyst sample, weighed accurately, of course, in nitric acid. Any insoluble material was filtered, ignited, and weighed. The filtrate was neutralized with ammonia until slightly basic and the formed $Al(OH)_3$ filtered hot and washed with a 1 per cent solution of NH_4NO_3. The $Al(OH)_3$ precipitate was ignited and weighed as Al_2O_3. From this data, the per cent of Al was calculated. The copper present in the catalysts could be determined in either of two ways. One was the gravimetric procedure of precipitating the copper with NaOH followed by ignition and weighing of the cupric oxide.

The volumetric method of copper determination was also used. After the dissolving of the alloy in HNO_3, titration with standard thiosulfate of the iodine released when potassium iodide is added to cupric solutions enables calculation of the per cent of copper.

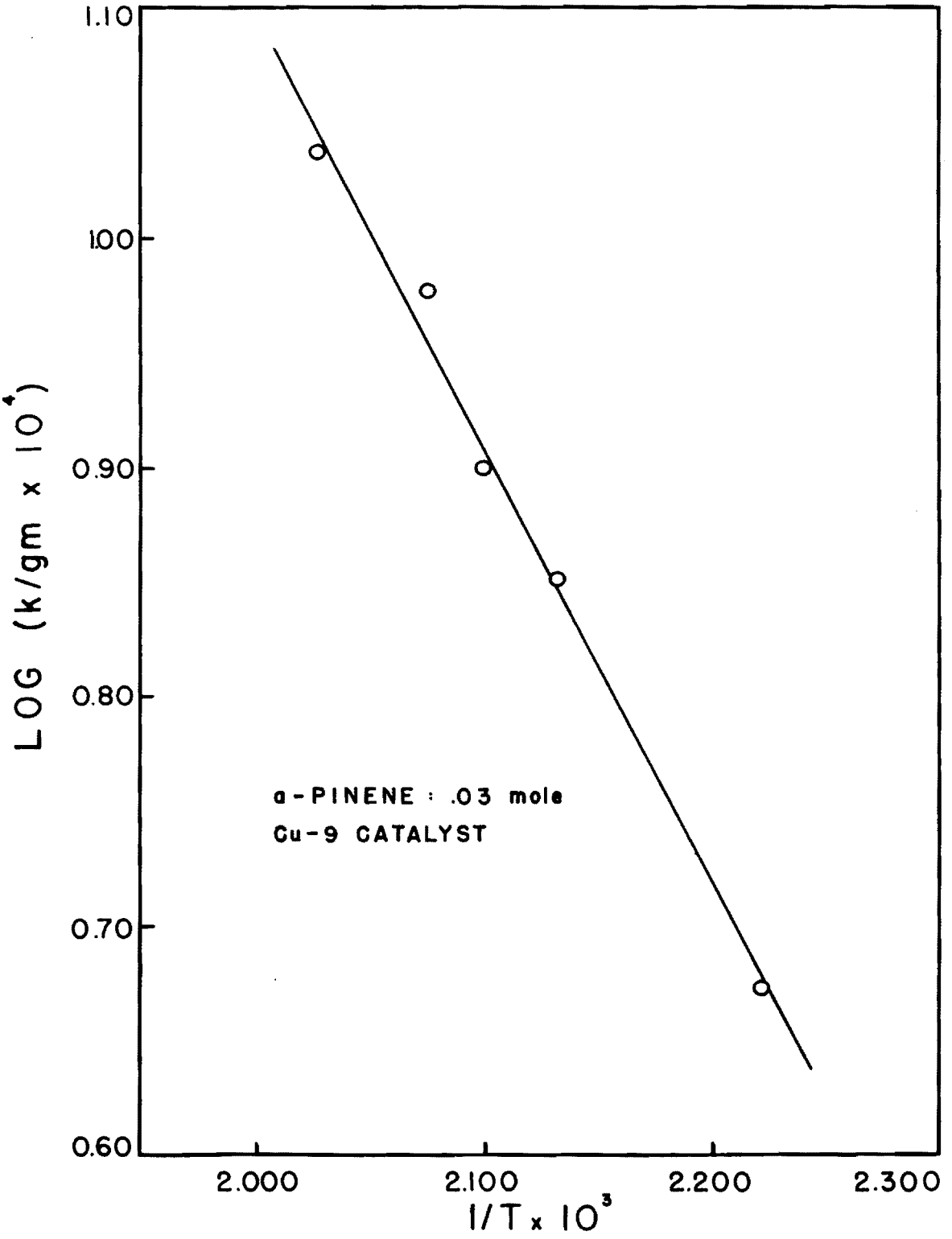

Figure 2. Energy of Activation Curve for α-pinene.

V RESULTS AND DISCUSSIONS

A. Effect of State of Division of the Alloy

From the data presented in Table II, below, it would appear that a more finely divided alloy is capable of producing a slightly more active catalyst. This is to be expected since in the more finely divided material, there would be a greater opportunity for removal of aluminum, and thus leaving a more finely divided copper catalyst having a somewhat greater surface area.

TABLE II

STATE OF DIVISION OF ALLOY

Catalyst Number[1]	Compound Being Hydrogenated	Temperature ° C	$k \times 10^4$ min^{-1}/g
R-Cu-1	5 ml acetone	109	10.08
R-Cu-1a	5 ml acetone	109	11.57
R-Cu-1	5 ml acetone	124	16.20
R-Cu-1a	5 ml acetone	124	19.50

1. For the symbolism used in this and succeeding tables, see Part IV, C, Preparation of the Catalyst.

The catalysts referred to in Table II were made from Devarda's alloy. The catalyst numbered R-Cu-1 was prepared from an alloy which had been ground in a mortar, while catalyst R-Cu-1a was prepared from an alloy ground in the Mikro-Pulverizer. The latter sample would pass through a 200-mesh screen, whereas the former sample for the most part was retained by a 100-mesh screen.

B. Effect of the Method of Preparation on Catalyst Activity

The methods for preparing each batch of catalyst has already been discussed in Part IV of this report.

Using the copper-aluminum ratio of 40-60 as the most satisfactory and practical, the next phase consisted of varying the method of preparations of the R-Cu-4 catalyst. This was considered necessary in order to determine whether or not significantly more active catalysts could be prepared. A similar concept has already been shown to be true in the case of the Raney nickel catalysts.[11]

TABLE III

VARIATION OF ACTIVITY OF CATALYST WITH PREPARATION METHOD

Hydrogenation of 5 ml of acetone at an initial pressure of 1000 ± 50 psi		
Catalyst Number	Temperature ° C	$\frac{k}{g} \times 10^4$ min^{-1}
R-Cu-4	127	25.1
R-Cu-4-4	127	61.0
R-Cu-4-6	127	42.9
R-Cu-4-7	127	87.1
R-Cu-4-4	112	39.8
R-Cu-4-8	112	40.8
R-Cu-4-9	112	39.8
R-Cu-4-4	97	24.1
R-Cu-4-8	97	23.1

---

11. H. Adkins and G. Billica, J. Am. Chem. Soc., 70, 695 (1948); H. Adkins and A. A. Pavlic, J. Am. Chem. Soc., 69, 3039 (1947); A. A. Pavlic and H. Adkins, J. Am. Chem. Soc., 68, 1471 (1946); L. W. Covert and H. Adkins, J. Am. Chem. Soc., 54, 9116 (1932); H. Adkins and H. R. Krsek, J. Am. Chem. Soc., 70, 412 (1948).

It appears, in general, that a slightly more active catalyst is formed whenever the time for the addition of the alloy to the caustic is decreased (i.e., the digestion time is speeded up), and whenever washing processes are rapidly achieved. The probable cause of this greater activity is due to a greater amount of hydrogen gas being held by the catalyst surface. This naturally would result since in order to decrease the digestion time it is necessary to cool very strongly the caustic so that the temperature may be held below 50° C. Keeping the temperature somewhat below 50° C. would enable a greater amount of hydrogen to be held by the surface.

In keeping with this, it has been observed that, on standing, the catalyst samples which were prepared in shorter time evolved more hydrogen more readily than did those catalysts prepared over a longer period of time, and at a somewhat higher temperature. In fact, it was necessary that these catalysts be stored in a refrigerator to prevent the undue loss of hydrogen gas.

The perhaps unexpected lesser activity of sample R-Cu-4-6 is not wholly unexpected in view of the fact that, in the preparation of this sample, too much cooling was used during the addition of the alloy to the caustic. As a result, much of the solution froze. When warmed slightly so as to melt the liquid, a considerable quantity of alloy was still found undigested and a rather vigorous reaction was started, and the solution began to froth and foam con-

siderably. The temperature also increased greatly. This rise in temperature, certainly well above 50° C, would cause hydrogen to be evolved more than in other cases where the temperature was controlled much better. It should also be noted, as will be discussed later, that this catalyst sample consisted of about equal parts of aluminum and copper. This, too, would be a likely cause for a lower activity of this sample.

C. Effect of the Copper-Aluminum Ratio on Catalyst Activity

One of the early phases of the work consisted in finding the ratio of copper to aluminum which, using the same method of preparation, would form the most active catalyst. Considering that it would be more economical not to use too small a ratio of copper to aluminum (resulting in too low a yield of catalyst weight per weight of alloy), it was decided that ranges of 40 to 60 per cent copper would be tried. Three different composition alloys containing 60, 50, and 40 per cent copper were prepared. Each alloy was converted by the same method and same controls to a Raney copper catalyst and each was then used to hydrogenate 5 ml of acetone or 5 ml of nitrobenzene at an initial pressure of 1000 ± 50 psi. From the data in Table IV, it is indicated that within the range covered, the alloy containing 40 per cent copper and 60 per cent aluminum is definitely superior to other compositions.

TABLE IV

COPPER-ALUMINUM RATIO IN ALLOYS

Catalyst Number	Composition	Hydrogen Acceptor	Temperature ° C	$\frac{k}{g} \times 10^4$ min^{-1}
R-Cu-2	60 Cu, 40 Al	5 ml acetone	127	7.41
R-Cu-3	50 Cu, 50 Al	5 ml acetone	127	21.61
R-Cu-4	40 Cu, 60 Al	5 ml acetone	127	25.1
R-Cu-2	60 Cu, 40 Al	5 ml nitro-benzene	127	2.37
R-Cu-3	50 Cu, 50 Al	5 ml nitro-benzene	127	3.39
R-Cu-4	40 Cu, 60 Al	5 ml nitro-benzene	127	4.51

This result is to be expected. It would seem reasonable to believe that in the case of larger amounts of aluminum, there would be formed in the new catalyst a greater surface area than would be obtained should the aluminum content be less. It should be pointed out, however, that the surface area is not the only factor which determines the catalytic activity, but it is a significant factor. One might also mention that the more aluminum and the more surface exposed, the greater would be the extent of adsorbed hydrogen.

It should also be pointed out that the copper-aluminum ratio of the catalyst itself might be expected to have some effect on the activity of the catalyst. As will be indicated in a later discussion of added elements to the alloy which appear in the catalyst, the effect these substances have is unpredictable.

In Table III the unexpected low activity of R-Cu-4-6 was pointed out. Because of the low activity and of the difficulties in the preparation of the sample, it was considered that perhaps the activity was low due to incomplete removal of aluminum by the digestion process. To check this, four different catalyst samples were analyzed for copper, aluminum, and insoluble materials. The results of these are presented in Table V.

TABLE V

ANALYSIS OF CATALYSTS

Catalyst Number	Per Cent Aluminum	Per Cent Copper	Per Cent Insolubles
R-Cu-4-4	5.50	93.5	1.01
R-Cu-4-6	49.6	47.6	2.20
R-Cu-4-7	34.3	65.9	Trace
R-Cu-4	4.9	93.2	1.6

It will be noted in the catalysts prepared using a long digestion period most of the aluminum has been removed. In the cases of a more rapid digestion period, the amount of aluminum removed is somewhat less. However, note in the sample which gave no difficulties during the digestion period (R-Cu-4-7) the copper aluminum ratio is almost 2:1. If one considers only the effect of the relative amounts of these two metals in the catalyst, the sample does show unexpected activity. It must be remembered, however, that through rapid washing and rapid digestion processes, considerably

more hydrogen has remained adsorbed on the surface. This would, according to Adkins, tend to increase the activity of the catalyst considerably.[12]

It is not believed, however, that this is a sufficient explanation in this case. Additional study regarding composition versus activity is indicated. It is quite possible for the aluminum not only to increase the surface of the catalyst, but also to cause an increase in the activation of the copper which would result in the latter being better able to adsorb and activate the hydrogen and/or hydrogen acceptor. If this would be true, one would expect there to be an amount of aluminum which would give maximum activation. Quantities both above and below this would tend to decrease the activity of the copper. Verification of this could be ascertained through preparation and analyses of other catalysts in which one would prepare catalysts containing various amounts of aluminum present in the catalyst itself. This likely could be done by preparing alloys of known composition, then preparing the catalyst in a system which could be used to measure the amount of evolved hydrogen. The digestion could be stopped at a predetermined amount of evolved hydrogen and the sample then washed in a uniform manner. The resulting catalyst would contain, therefore, the approximate amount of aluminum desired.

---

12. H. Adkins and J. Krsek, J. Am. Chem. Soc., 70, 412 (1948).

D. Effect of Other Elements in Alloy and in Catalyst

This phase of the study is quite incomplete at the present time, and not all of the desired elements have been incorporated into alloys or catalysts. Table VI shows several results thus far obtained.

TABLE VI

EFFECT OF ELEMENTS ADDED TO ALLOYS OR CATALYSTS

Hydrogenation of 5 ml of Acetone at an Initial Pressure of 1000 ± 50 psi

Catalyst Number	Alloy Composition in Per Cent	Temperature ° C	$\frac{k}{g} \times 10^4$ min^{-1}
R-Cu-1A	50 Cu, 45 Al, 5 Zn	157	43.32
R-Cu-3	50 Cu, 50 Al	157	48.62
R-Cu-Ni-2	25 Cu, 25 Ni, 50 Al	98.5	12.4
R-Cu-Ni-3	40 Cu, 10 Ni, 50 Al	98.5	13.6
R-Cu-Ni-4	10 Cu, 40 Ni, 50 Al	99	21.2
R-Cu-3	50 Cu, 50 Al	98.5	20.2[1]
R-Cu-4	40 Cu, 60 Al	98.5	26.6
R-Ni-1	Commercial Raney Ni alloy	98.0	70.4

1. Calculated at this temperature by using the Arrhenius equation.

No conclusions can as yet be drawn from these fragmentary results. Considerable work is needed if one is to be able to interpret possible effect of various elements on the copper catalyst. For instance, it would be desirable to substitute more zinc for some of the aluminum for comparison with Devarda's alloy catalysts.

The element tin should also be included as a substitute for some of or all of the aluminum. In this case one may experience some difficulties removing the tin from the alloy due to the physical conditions of the bronze alloy.

For the above table, however, it is interesting to note that even though Raney nickel is a more effective catalyst for the hydrogenation of acetone than is Raney copper catalysts, the catalyst made from any copper-nickel combination is not as active as the Raney copper catalyst R-Cu-4. Note also that the 40:10 copper-nickel ratio is only slightly more effective than the 25:25 alloy.

Continuation of this phase of the work is in progress.

E. Effect of Ageing of Catalysts.

It has been observed that upon standing over a period of time, the activity of a given Raney catalyst decreases. This is amply illustrated in the table below.

TABLE VII

AGEING OF CATALYSTS

Hydrogenation of acetone, 5 ml, at an Initial Pressure of 1000 ± 50 psi			
Catalyst Number	Date of Hydrogenation	Temperature ° C	$\frac{k}{g} \times 10^4$ min^{-1}
R-Cu-4-6	1-26-55	134	52.5
R-Cu-4-6	9-15-55	134	26.5
R-Cu-4-6	1-26-55	121	35.9

(continued)

TABLE VII (Continued)

AGEING OF CATALYSTS

Catalyst Number	Date of Hydrogenation	Temperature ° C	$\frac{k}{g} \times 10^4$ min^{-1}
R-Cu-4-6	9-16-55	121	20.6
R-Cu-4-7	2- 1-55	137	113.0
R-Cu-4-7	9-16-55	137	61.1
R-Cu-4-7	2- 1-55	122	77.1
R-Cu-4-7	9-13-55	122	38.5
R-Cu-4-4	1-20-55	125	57.8
R-Cu-4-4	7-12-55	125	25.7
R-Cu-4-4	1-20-55	111	39.6
R-Cu-4-4	5-10-55	111	17.3

In every case there was considerable loss in activity of the catalyst upon standing. This loss, in general, was of the order of 50 per cent over a period of six to eight months. In order to have a little clearer picture as to whether or not the loss will continue at this rate, these catalysts will be checked again in February, 1956.

The exact cause of loss of activity is not specifically known, although it is probably due to changes of the surfaces of the catalysts as well as to loss of adsorbed hydrogen.

F. Energy of Activation

As pointed out previously, by determination of the rate constant at various temperatures, one can obtain, graphically, activa-

tion energies of the particular hydrogenation processes. Table VIII gives a summary of the energies of activation obtained in this work.

TABLE VIII

ACTIVATION ENERGIES AND RATE CONSTANTS

In Each Case 5 ml of Compound Was Used at an Initial Hydrogen Pressure of 1000 ± 50 psi			
Compound	Catalyst Number	Activation Energy, cal/mol	$\frac{k}{g} \times 10^{4}$ min^{-1} (at 127° C)
Acetone	R-Cu-4-4	8900	61.0
Acetone	R-Cu-4-6	9350	42.9
Acetone	R-Cu-4-7	7870	87.1
Acetone	R-Ni	6300	127.4
Allyl alcohol	R-Cu-4-9	6600	33.9
Benzaldehyde	R-Cu-4-9	7060	30.9
Butyronitrile	R-Cu-4-7	9390	Note 1
Cyclohexene	R-Cu-4-8	1440	3.84
d-Limonene	R-Cu-4-9	5310	4.98
Mesityl oxide	R-Cu-4-9	8460	55.4
1-Nitropropane	R-Cu-4-7	11000 (Note 2)	16.5
2-Pentene	R-Cu-4-9	4300	10.06
a-Pinene	R-Cu-4-9	8720	1.40
Propionaldehyde	R-Cu-4-9	14700	23.3
Styrene	R-Cu-4-7	14950	242.6
Styrene	R-Cu-4-8	11000	328.9

NOTES

1. Butyronitrile gave no detectable reaction at even 140° C. At 212 the rate constant was found to be 29.8 x 10^{-4} $min^{-1}g^{-1}$.

2. This value was determined by the use of R-Ni catalyst as well as R-Cu-2 catalyst.

In addition to those compounds listed in Table VIII, several other compounds were studied, but due to these materials not hydro-

genating or the process being nonreproducible, no activation energies were calculated. These substances are summarized in Table IX.

TABLE IX

COMPOUNDS FOR WHICH NO

ACTIVATION ENERGIES WERE OBTAINED

Compound	Catalyst Used	$\frac{k}{g} \times 10^4$ min^{-1}	Remarks
t-Cinnamic Acid	R-Cu-4-8	5.10 at 89° C	Ethanol as solvent
	R-Cu-4-8	0.893 at 125° C	Benzene as solvent
1,3-Cyclohexadiene	Failed to hydrogenate		
Ethyl Oleate	Failed to hydrogenate		
Fumaric Acid	R-Cu-4-8	No reaction at 194° C	
Maleic Anhydride	R-Cu-4-8	3.03 at 160° C	n-Hexane as solvent
	R-Cu-4-8	3.32 at 202° C	n-Hexane as solvent
2-Methyl-2-butene	R-Cu-4-8	Failed to hydrogenate at 71° C	
Nitrobenzene	R-Cu-4-6	9.9 at 137° C	
	R-Cu-4-4	10.4 at 123° C	

G. Nature of the Organic Compound

Each of the compounds listed in Tables VIII and IX will be mentioned individually so that any pecularities which were noticed may be mentioned.

1. Acetone

This compound was hydrogenated readily to isopropyl alcohol, even at temperatures as low as 83° C where the rate constant was 26.4 min^{-1} x 10^{-4}/g.

2. Allyl Alcohol

The alcohol gave n-propyl alcohol upon hydrogenation. The reaction occurred readily and the yields were good.

3. Benzaldehyde

Initially this compound gave poor results. It was observed that the catalyst turned quite red after the hydrogenation. The results from run to run were not usually reproducible. Later it was found, however, that excellent results could be obtained if the benzaldehyde were freshly distilled, just prior to its use. In such cases, the catalyst did not change during the reaction and the results were readily reproducible. Further, these were due apparently to benzoic acid contamination. In the presence of small amounts of this acid, the rate constant at 127° C was only 5.11×10^{-4} $min^{-1}g^{-1}$ as compared to 30.9×10^{-4} $min^{-1}g^{-1}$ for the pure material.

4. Butyronitrile

After attempting hydrogenation of this compound at lower temperatures (without success), it was observed that hydrogenation could be affected slowly and incompletely, even at 200° C. However, the catalyst after these runs was red. Ammonia was detected in the gas vented at the conclusion. Tests of the gaseous materials for butane gas were unsuccessful. Attempts to isolate any significant amounts of products from the various runs were unsuccessful. Dis-

tillation of the product yielded 2.5 ml of starting material, 0.2 ml of material boiling from 75° to 79° C (ethanol and butyl amine), and 0.5 ml of a mixture, boiling from 79° to 111° C.

5. Cyclohexene

Faucounau has reported that Raney Cu will not hydrogenate cyclohexene. This is somewhat unexpected since this molecule has an isolated double bond and shows several reactions of the double bond. In this work cyclohexene was only very slowly reduced at 75° C ($k \times 10^4$ $min^{-1}g^{-1}$ is 2.8). Also unusual was the extremely low activation energy which means that the rate constant changes only slightly with the temperature. At 163° C, the rate constant was 5.34×10^{-4} min^{-1}/g. One great difficulty noted when working with this material was that any slight fluctuation in temperature could invalidate any result.

6. 1,3-Cyclohexadiene

This compound did not hydrogenate at low temperature and it was not tried above 100° C.

7. t-Cinnamic Acid

This compound resisted hydrogenation. The catalyst also was changed in appearance after attempted reaction. The compound did reduce very slowly, however, in ethanol as a solvent. In benzene the rate of the reaction was almost too slow to determine. The reaction in ethanol was found to yield an indication of ester present.

8. Ethyl Oleate

The ester failed to react at 123° C. Since the sample on hand was likely too impure to work further, no additional attempts were tried on this compound.

9. Fumaric Acid

Hydrogenation did not occur even at temperatures up to 194° C.

10. d-Limonene

This was found to hydrogenate slowly at temperatures as low as 150° C. The usual practice of permitting the hydrogenation to run only until sufficient readings could be obtained to give the rate constant was followed in preliminary runs. Usually the reaction was stopped at 25 to 35 per cent completion. For a typical run, from the amount of hydrogen taken up, it was calculated that 30 per cent of the starting compound could have been reduced to d-carvomenthene , or 15 per cent of it could have been reduced to p-menthane. Distillation of the product of the interrupted hydrogenation gave a 70 per cent yield of a fraction boiling at 175° to 176° C and 30 per cent yield of a fraction boiling at 178° to 181° C. These fractions corresponded to d-limonene (b.p. 176.9) and d-carvomenthene (b.p. 179.0), respectively.

Additional runs, stopping the hydrogenation at various other pressure drops were analyzed also. Runs were made where 86 psi was

absorbed during the reaction (in No. 200); 250 psi in No. 201; 260 psi in No. 202; 320 psi in No. 203; 312 for 5 ml of material in No. 205 and 517 psi for 5 ml in No. 206. These runs were then analyzed by either hydrogen uptake method or by the method of Uhrig and Levin[13], which is based on titration of the reaction product with a 3 per cent bromine in acetic acid solution. Polarimeter readings were also taken on the various products as they were isolated. The results of these experiments are tabulated in Table X.

TABLE X

ANALYSIS OF HYDROGENATION

PRODUCTS FROM D-LIMONENE RUNS

Sample Run	Titre	Average Titre	Per Cent Unreacted	Per Cent Reacted	Polarimeter Reading	Per Cent Reacted by H_2 Pressure
Unreacted	4.25					
Unreacted	4.25	4.25	100	0	13.30	0
Hyd. 200	3.65					
Hyd. 200	3.85	3.75	88.2	11.8	12.40	12.2
Hyd. 201	2.78					
Hyd. 201	2.72	2.75	64.7	35.3	12.00	33.6
Hyd. 202	2.54					
Hyd. 202	2.66	2.60	61.2	38.8	11.75	37.6
Hyd. 203[1]	2.21					
Hyd. 203[1]	2.29	2.25	53.0	47.0	11.30	47.0
Hyd. 205	2.22					
Hyd. 205	2.24	2.23	51.5	48.5	11.60	45.9
Hyd. 206	1.15					
Hyd. 206	1.15	1.15	75.0	25.0	5.35	75.7

1. The calculation based on the pressure used for Hydrogenation 203 as being enough to react 47 per cent, a figure taken from the bromine titration.

13. K. Uhrig, and H. Levin, Ind. Engr. Chem. Anal. Ed. 13, 90 (1941).

A plot of the polarimeter reading versus the per cent reacted gives a curve which changes slope at 50 per cent reaction, indicating a two-step reaction. The first step is the hydrogenation of the exo-bond of d-limonene producing d-carvomenthene which is then reduced further but with a decreased rate. If the reaction were indiscriminate as to which bond was being reduced, the optical activity would produce a straight line from the 0 per cent reduction to the 100 per cent reduction instead of the broken line.[14]

The rate constant for R-Cu-4-9 with d-limonene is 12.91 while the rate constant for hydrogenation of d-carvomenthene is 6.87, both being taken at 194° C.

11. Maleic Anhydride

This compound was hydrogenated with difficulty, being only slowly converted to the saturated dibasic acid.

12. Mesityl Oxide

Study was undertaken on this compound since it possesses a conjugated carbon-carbon double bond with a carbonyl grouping. Interest was centered in which of these two points of possible attack would be the first to hydrogenate, or whether the reaction were purely a random hydrogenation.

In one hydrogenation, 5 ml of mesityl oxide was reduced using R-Cu-4-9 as the catalyst. Distillation of the product gave a yield

---

14. J. F. Fuzek and H. A. Smith, J. Am. Chem. Soc., 70, 3743 (1948).

of 80 per cent recovery of the 5 ml or 87 per cent recovery from the contents of the liner after the reaction. The product boiled at 114.0° to 115.5° and appears to be 4-methyl-pentanone-2. From another hydrogenation was recovered 1.5 ml of 4-methyl-pentanone-2 together with some mesityl oxide and probably a little alcohol, 4-methyl-pentanol-2. The two yields were treated with 90 per cent sulfuric acid to yield 0.43 ml and 0.27 ml of unsaturated material out of 4.4 and 4.0 ml respectively. From the latter hydrogenation one calculates there is 38.0 per cent of 4-methyl-pentanone-2, 6.8 per cent of 4-methyl-pentanol-2 and 55.2 per cent mesityl oxide. According to the hydrogen uptake one would calculate a percentage of 55.3 unreacted carbonyl.

From the other hydrogenation, the hydrogen uptake would indicate 8 per cent unreacted carbonyl group. Distillation gave 86 per cent of 4-methyl-pentanone-2, 9.5 per cent of 4-methyl-pentanol-2 and 4.5 per cent mesityl oxide. Using the amount of hydrogen necessary to hydrogenate acetone as a basis, the amount of hydrogen used up is enough to hydrogenate all but 8 per cent of the carbonyl groups in the material if no double bonds are hydrogenated.

Thus again it would appear that this is another reaction which occurs as a two-step process.

13. Nitrobenzene

Nitrobenzene was converted to aniline although some difficulty obtaining reproducible results was observed. The temperature

necessary to effect the reaction was somewhat above that required for acetone. The catalyst was changed in appearance after being in contact with the reaction mixture, being somewhat darker in color. It appears likely that the copper is, to a small extent at least, oxidized by the nitrobenzene. The darkened catalyst also gained slightly in weight. In sulfuric acid solution (dilute) the changed catalyst was found to react slightly and to give a positive test for the $Cu(NH_3)_4^{++}$ ion. After the acid treatment, the catalyst was restored to its former brighter color.

14. 1-Nitropropane

Conversion of the aliphatic nitro compound to the amine was achieved readily and in good yields. No difficulties such as those described for nitrobenzene were observed.

15. 2-Pentene

The olefin was hydrogenated to pentane. Commercial 2-pentene failed to hydrogenate although that prepared in the lab (previously described) hydrogenated to the paraffin satisfactorily.

16. α-Pinene

This compound when hydrogenated with sufficient hydrogen to form 35 per cent of the saturated product was found to yield pinane in 30 per cent actual yield, or a conversion of 85 per cent of the expected quantity.

17. Propionaldehyde

Propyl alcohol was obtained in good yields and without difficulties by the hydrogenation process.

18. Styrene

Styrene was converted to ethyl benzene in 81 per cent yield. A small amount of poly-styrene was also obtained.

Respectfully submitted:

James A. Stanfield
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

Paul K. Calaway, Director
Engineering Experiment Station

BIBLIOGRAPHY

1. Adkins, H., Reactions of Hydrogen with Organic Compounds Over Copper-Chromium Oxides and Nickel Catalysts, (Madison: The University Press), p. 9.

2. Adkins, H. and Billica, G., J. Am. Chem. Soc., 70, 695 (1948).

3. Adkins, H. and Krsek, H. R., J. Am. Chem. Soc., 70, 412 (1948).

4. Adkins, H. and Pavlic, A. A., J. Am. Chem. Soc., 69, 3039 (1947).

5. Covert, L. W. and Adkins, H., J. Am. Chem. Soc., 54, 4116 (1932).

6. Faucounau, L., Bul. soc. chim., 5, 4, 58 (1937).

7. Fuzek, J. and Smith, H. A., J. Am. Chem. Soc., 70, 3743 (1948).

8. Hachihama, Y., Kawata, K., Imoto, M., J. Soc. Chem. Ind., Japan, 45, 297 (1942).

9. Mozingo, R., Organic Syntheses, Coll. Vol. III (New York, John Wiley and Sons, Inc.), p. 181.

10. Mechelin, V., and Jingera, J. C., Bul. soc. chim. Belges, 59, 597 (1950).

11. Pavlic, A. A., and Adkins, H., J. Am. Chem. Soc., 68, 1471 (1946).

12. Raney, M., U. S. Patent 1,564,787 (Dec., 1925).

13. Raney, M., U. S. Patent 1,628,190 (May, 1927).

14. Raney, M., U. S. Patent 1,915,473 (June, 1933).

15. Raney, M., Ind. Engr. Chem., 32, 1199 (1940).

16. Smith, H. A. and Fuzek, J. F., J. Am. Chem. Soc., 70, 3743 (1948).

17. Smith, H. A. and Pennekamp, E. F. H., J. Am. Chem. Soc., 67, 276 (1945).

18. Smith, H. A., Alderman, D. M., and Nadig, F. W., J. Am. Chem. Soc., 67, 272 (1945).

19. Smith, H. A. and Stanfield, J. A., J. Am. Chem. Soc., 71, 81 (1949).

20. Uhrig, K. and Levin, H., Ind. Engr. Chem. Anal. Ed., 13, 90 (1941).

21. Weiser, H. B., Colloid Chemistry (New York: John Wiley and Sons, Inc., 1946) p. 51.

DISTRIBUTION LIST

Agency	No. of Copies
Commanding General, Ordnance Weapons Command Rock Island, Illinois Attn: Research Branch	2
Commanding Officer, Office of Ordnance Research Box CM, Duke Station Durham, North Carolina	10
Chief of Ordnance, Department of the Army Washington 25, D. C. Attn: ORDTB-PS	2
Office of Naval Research Washington 25, D. C.	1
Commanding General Aberdeen Proving Ground, Maryland Attn: Tech Info Div	1
Commanding General Redstone Arsenal Huntsville, Alabama	1
Commanding Officer, Picatinny Arsenal Dover, New Jersey	1
Commanding Officer, Rock Island Arsenal Rock Island, Illinois	1
Commanding General, Research & Engineering Command Army Chemical Center, Maryland	1
Commanding Officer, Watertown Arsenal Watertown 72, Massachusetts	1
Commander, U. S. Naval Proving Ground Dahlgren, Virginia	1
Chief, Bureau of Ordnance (AD3) Department of the Navy Washington 25, D. C.	1
U. S. Naval Ordnance Laboratory White Oak, Silver Spring 19, Maryland Attn: Library Division	1

Agency	No. of Copies
Director, National Bureau of Standards Washington 25, D. C.	1
Corona Laboratories, National Bureau of Standards Corona, California	1
Commanding Officer, Frankford Arsenal Bridesburg Station, Philadelphia, Pennsylvania	2
Technical Information Service P. O. Box 62, Oak Ridge, Tennessee Attn: Reference Branch	1
The Director, Naval Research Laboratory Washington 25, D. C. Attn: Code 2021	1
Director, Applied Physics Laboratory Johns Hopkins University 8621 Georgia Avenue, Silver Spring 19, Maryland	1
Commanding General, Air University Maxwell Air Force Base, Alabama Attn: Air University Library	1
Chief, Birmingham Ordnance District 2120 Seventh Avenue, North, Birmingham 3, Alabama	2
Commanding Officer, Office of Naval Research Branch Office, Navy, 100, FPO, New York, New York	1
Chief of Ordnance, Department of the Army Washington 25, D. C. Attn: ORDGU-SE FOR TRANSMITTAL TO: Canadian Joint Staff 2001 Connecticut Ave., N. W., Washington 25, D. C. Thru: ORDGU-SE	1
U. S. Atomic Energy Commission, Document Library 19th & Constitution Ave., Washington 25, D. C.	1

Agency	No. of Copies
Commanding General, Air Res. & Dev. Command P. O. Box 1395, Baltimore 3, Maryland Attn: RDR	1
Commanding General, Air Res. & Dev. Command P. O. Box 1395, Baltimore 3, Maryland Attn: RDD	1
Armed Services Technical Information Agency Document Service Center Knott Building, Dayton 2, Ohio Attn: DSC-SD	5
Scientific Information Section, Research Branch Research & Development Division Office, Assistant Chief of Staff, G-4 Department of the Army, Washington 25, D. C.	1
NAC for Aeronautics 1724 F Street, N. W., Washington 25, D. C. Attn: Mr. E. B. Jackson, Chief Office of Aeronautical Intelligence	1